ethyline, propene, vinylacetylene, and butadiene all were ruled out after consultation with literature spectra. 1-Butene in the gauche form was selected after comparison to its literature spectra. Of our possible unassigned product bands from the CH₃-C=C-CD₃ photolysis at 883.1, 839.2, 807.2, and 790.3 cm⁻¹, the band at 839.2 cm⁻¹ surely must correspond to the R=C=CHD out-of-plane bend because the kinetic behavior is type II. No literature source was available for CH₃CH₂CH=CHD, but it compares favorably with the frequency for the corresponding mode in ethylene in xenon at 839.5 cm⁻¹. 8

Kinetics. The structural assignments combined with the kinetic behavior now provide us with the information that methane and propene are formed simultaneously. 1-Butene is formed along another pathway. Acetylene is formed most rapidly at all concentrations. This must be due to its formation in reactions I and II, and possibly a third reaction.

Relative Product Yield. The distribution of two acetylene molecules per reaction between the two bimolecular reactions can now be explained by considering relative absorbance ratios after approximately 10% photolysis of 2-butyne. The ratio of the band heights for methane:propene:acetylene:propyne is 1:1:4:10 at M/R = 1/50 and 1:2:10:10 at M/R = 1/300. It can be seen that an approximately 2-fold enhancement of the formation of butene and acetylene occurs upon dilution from M/R = 1/50 to 1/300.

Conclusion

The ultraviolet-region singlet photochemistry of gas-phase 2-butyne is known to result from the primary step of C=H bond breakage. 2 All of the reported products are due to recombination of the 2-butyne fragments and, presumably, the formation of molecular hydrogen. 2 The formation of acetylene in our experiments may be considered to arise from the elimination of molecular hydrogen from a triplet-excited 2-butyne monomer unit according to

CH₃-C≡C-CH₃ → CH₃-C≡C-CH + H₂

followed by

CH₃-C≡C-CH → [CH=CH-CH=CH] → 2C₂H₂

Alternatively, the photoreaction of two 2-butyne molecules or a higher aggregation in a xenon cage would involve the concerted formation of [CH=CH-CH=CH] and butene to give the overall reaction:

2CH₃-C≡C-CH₃ → CH₄ + CH₃-C≡C-H + 2H-C≡C-H path I

2CH₃-C≡C-CH₃ → CH₃-C=CH-CH₃ + 2H-C≡C-H path II

The idea that acetylene may be formed from monomer 2-butyne and from two or greater numbers of aggregated 2-butyne molecules is consistent with Figure 3, which shows acetylene in at least four different concentration-dependent sites. Furthermore, the isotope scrambling would be correct for all three reactions.

Evidence that the mechanism described above does not occur from singlet excitation comes indirectly from the fact that we did not see a photoreaction from propyne/Xe (M/R = 1/100) or from propyne/Ar (M/R = 1/100) using the same experimental conditions. Reactions are known to occur in the gas phase, initiated by singlet-state C=H bond breakage. 8 Presumably the singlet mechanisms have lower quantum yield in the matrix, perhaps due to cage recombination and/or a lower singlet transition probability in xenon.

Although lifetime studies on electronically excited molecules have demonstrated the external heavy atom spin–orbit coupling effect by xenon, relatively few studies have demonstrated the effect on the photochemical outcome. Studies by Warren et al., 2 Collins and Pimentel, 4 Kelley and Rentzepis, 5 Rasanen, 11 and Laursen and Pimentel 6 all demonstrate product differences. Presumably the different photoproducts form along triplet and singlet potential surfaces, which can be selected by choosing xenon or argon, respectively.

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Period Doubling and Chaos in a Three-Variable Autocatalator

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A three-variable extension of the classical two-variable autocatalator is presented as a prototype for complex dynamical behavior in isothermal chemical reactions. The model is closely related to recent extensions of the autocatalator involving temperature feedback. Period doubling and chaos with periodic windows are found on varying a bifurcation parameter. The bifurcation sequence is a remerging Feigenbaum tree, with period doubling leading to chaos followed by a reverse sequence leading back to period 1.

Introduction

The two-variable autocatalator model for isothermal reaction in a thermodynamically closed system has been used successfully to reproduce many typical features of chemical oscillations. 1-3 This scheme considers the conversion of a chemical precursor P

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Introduction

The two-variable autocatalator model for isothermal reaction in a thermodynamically closed system has been used successfully

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to a final product C via two reactive intermediates A and B, through the sequence of steps

\[
P \rightarrow A \quad \text{rate} = k_{dp} \quad (0)
\]

\[
A \rightarrow B \quad \text{rate} = k_{da} \quad (U)
\]

\[
A + 2B \rightarrow 3B \quad \text{rate} = k_{ab} \quad (1)
\]

\[
B \rightarrow C \quad \text{rate} = k_{bc} \quad (2)
\]

The conditions for oscillation, etc. can be obtained analytically when the precursor concentration is considered to be constant. If a slow, exponential decay of the precursor is included, the length of the preoscillatory (induction) period and of the oscillatory phase, including the number of oscillations, can also be estimated accurately.

Recently, Scott and Tomlin\textsuperscript{4,5} have begun an investigation of the effects of thermal feedback on this scheme by allowing reaction 2 to be exothermic and the rate constant for the precursor decay step (0) to have an Arrhenius temperature dependence. Self-heating due to the reaction is then coupled internally to the kinetic mechanism, providing a three-variable system. Generic behavior, including period doubling, mixed-mode oscillations, and chemical chaos can all be found for suitable parameter values in the pool chemical formulation, and transient chaos appears when reactant consumption is admitted. As well as the coupling, the Arrhenius form provides a second nonlinearity. Gray and Kay\textsuperscript{6} have demonstrated that the latter is not a vital component: most of the above features arise with a linear temperature dependence.

In this paper we consider a different modification of the autocatalator—chemical rather than thermal—that produces a three-variable, isothermal scheme capable of supporting complex periodic and aperiodic responses. Additional steps are invoked involving the species C: first, a catalysis of the induction step from P to A, and second a simple decay of C to the new final product D. Thus, the model becomes

\[
P \rightarrow A \quad \text{rate} = k_{dp} \quad (0)
\]

\[
P + C \rightarrow A + C \quad \text{rate} = k_{pc} \quad (C)
\]

\[
A \rightarrow B \quad \text{rate} = k_{da} \quad (U)
\]

\[
A + 2B \rightarrow 3B \quad \text{rate} = k_{ab} \quad (1)
\]

\[
B \rightarrow C \quad \text{rate} = k_{bc} \quad (2)
\]

\[
C \rightarrow D \quad \text{rate} = k_{ec} \quad (3)
\]

With a constant precursor concentration \( p_0 \), the rate equations for the three intermediates are

\[
\frac{da}{dt} = k_{dp} p_0 + k_{pc} c - k_{a} a - k_{ab} b \quad (4a)
\]

\[
\frac{db}{dt} = k_{a} a + k_{ab} b - k_{bc} c \quad (4b)
\]

\[
\frac{dc}{dt} = k_{bc} c - k_{ec} c \quad (4c)
\]

Rewriting these equations in a suitable dimensionless form gives the three-variable, four-parameter set

\[
\frac{da}{dt} = \sigma + \mu \gamma - \alpha \beta^2 - \alpha \quad (5a)
\]

\[
\sigma \frac{d\beta}{dt} = \alpha \beta^2 + \alpha - \beta \quad (5b)
\]

\[
\delta \frac{d\gamma}{dt} = \beta - \gamma \quad (5c)
\]

with

\[
\alpha = (k_{a} k_{bc})^{1/2} a, \quad \beta = (k_{a} k_{bc})^{1/2} b
\]

\[
\gamma = (k_{a} k_{p} k_{bc})^{1/2} c, \quad \tau = k_{dp} t
\]

\[
\kappa = (k_{a} k_{p} k_{bc})^{1/2} p_0, \quad \delta = k_{a} k_{p} k_{bc}
\]

Before eqs 5a–c are generally considered, a number of limiting cases can be discussed. As \( \mu \to 0 \), corresponding to \( k_a \) vanishing, species C no longer couples back to the classical autocatalator reactions. In this limit, eqs 5a, b provide an independent, two-variable system with Hopf bifurcations at

\[
x^2 = \left[1 - 2 \sigma \pm (1 - 8 \sigma)^{1/2}\right]/2 \sigma \quad (6)
\]

for \( \sigma < 1/4 \), giving rise to stable period-1 oscillations only.\textsuperscript{1,2}

The limit \( \kappa \to 0 \), with finite \( \mu \), removes the uncatalyzed initiation step. This system of equations is of interest for modeling constant-velocity reaction-diffusion waves, as we pursue elsewhere.

If either or both \( \sigma \) and \( \delta \) become small, the corresponding species B and C become "fast variables", allowing the resulting dynamics to be interpreted in terms of reduced schemes and lower dimensional manifolds.

Results

To illustrate the behavior of the full system, we consider the parameter values \( \kappa = 10, \beta = 2 \times 10^{-3} \), and \( \sigma = 5 \times 10^{-3} \). The concentration of the precursor is the most easily varied experimental parameter (indeed it will automatically vary during the course of any real experiment because of the slow reactant consumption); however, varying \( p_0 \) affects both \( \mu \) and \( \kappa \) in the above formulation. We choose to vary only \( \mu \); if desired, \( p_0 \) can be varied by maintaining the ratio \( \kappa/\mu \) constant in the overall initiation rate \( \kappa + \mu \gamma \) in eq 5a.

Figure 1 shows six representative time series for increasing values of \( \mu \). The responses are period 1, period 2, period 4, period 8, chaos, and period 5. Such a sequence is symptomatic of a period-doubling route to chaos followed by periodic windowing.\textsuperscript{7-10} The strange attractor formed in concentration phase space by the chaotic motion is displayed in Figure 2a. The period-5 limit cycle is shown in Figure 2b. The bifurcation structure of this model can be summarized in more detail and over a wide range of the parameter \( \mu \) by considering the intersections of the attractor with a suitable Poincaré section in this phase space. A particularly convenient section is defined by the maximum or minimum in \( \gamma \), with \( \gamma = \beta \) according to eq 5c. Choosing the minimum in \( \gamma \) and varying \( \mu \) leads to the Feigenbaum cascade shown in Figure 3.

Rather than the typical period-doubling sequence seen in many simple maps and continuous systems, the sequence in Figure 3 develops to chaotic responses and then reverses. On reaching the period-5 window, period doubling gives rise to period 10, and then an inverse Feigenbaum tree emerges in which the system eventually returns to period 1. Reemerging Feigenbaum trees have been found in maps and continuous systems with more than one parameter.\textsuperscript{11} We will report elsewhere on the dependence of these features on the parameters of eqs 5.

Discussion

The first chemically consistent model, in the sense that species concentrations do not become negative and the rate equations have "law of mass action" form, to show chaos was that of Willamowski and Rössler.\textsuperscript{12,13} Their three-variable scheme, involving 10 reactions and 5 pool chemical species, is an adaptation of the Lotka–Volterra model with a third, switching variable. It is not clear that mass conservation (reactant consumption) can be admitted in the same simple way that it enters the present scheme or that the chaotic patterns would be retained as transient behavior.

Hudson and Rössler\textsuperscript{14} used an approach similar to that followed here. They considered a two-variable oscillator based on quadratic autocatalysis and a Michaelis-Menten decay reaction. A buffer step was then introduced through which one of the original variable species could be reversibly converted to a third variable species. This extra step provides a route for internally varying a system "parameter" in much the same way as species C in the present scheme affects the overall initiation rate $k + \mu \gamma$ via step C.

Wasserman and co-workers\textsuperscript{15} have used a nonlinear transfor-

\textsuperscript{14} Hudson, J. L.; Rössler, O. E. Modelling of Patterns in Space and Time, Jäger, W., Murray, J. D., Eds.; Springer-Verlag: Berlin, 1984; pp 135-145.

formation to convert a number of nonchemical models like the forced Duffing equation and the Lorenz system into schemes that obey mass-action kinetics. The transformation does not alter the qualitative features of a particular model, thus allowing known dynamic features to be applied to a corresponding chemical system. The chemical mechanisms derived from the dynamic equations, however, do not have the simplicity of the scheme presented here.

The similarity of the behavior of the present isothermal scheme and that of the nonisothermal autocatalator can be formalized through an alternative scaling of eqs 4. With

\[
\begin{align*}
\alpha &= (k_1/k_2)^{1/2}a, \\
\beta &= (k_1/k_2)^{1/2}b, \\
\gamma &= k_{c}/k_0, \\
\tau &= k_{ct}
\end{align*}
\]

\[
\mu = (k_1k_0^2/k_1k_2^2)^{1/2}p, \\
\nu = k_a/k_2
\]

the equations become

\[
\begin{align*}
\frac{d\alpha}{d\tau} &= \mu(1 + \gamma) - \alpha\beta^2 - \nu\alpha \\
\frac{d\beta}{d\tau} &= \alpha\beta^2 + \nu\alpha - \beta \\
\frac{d\gamma}{d\tau} &= \xi\beta - \chi\gamma
\end{align*}
\]

This is the same form as the linearized temperature dependence model of Gray and Kay\(^6\) in which \(\gamma\) represents the dimensionless degree of self-heating. The terms on the right-hand side of (7c) are the rates of chemical heat evolution and Newtonian heat transfer. In this sense, the catalysis in step C mimics the enhancement of the initiation rate due to self-heating, and the decay of C in step 3 is equivalent to Newtonian cooling. The limit \(k_3 \rightarrow 0\) would correspond to making the nonisothermal system adiabatic.

The three-variable autocatalator presented here as well as its nonisothermal cousins\(^4\)\(^6\) are attractive models for developing a better understanding of complex oscillations and chaos in chemical systems. The models are direct descendants of the well-developed two-variable autocatalator, and the complex behavior can be related in a straightforward manner to the behavior of the simpler model. The three-variable extensions maintain the conservation features of their two-variable parent. In addition to the period-doubling sequence reported here, mixed-mode oscillations that transform into chaotic responses are also exhibited.\(^4\)\(^6\) The simplicity of the three-variable autocatalator will allow systematic and detailed analyses of several types of complex dynamical behavior.

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